PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-213651
(43)Date of publication of application : 20.08.1996

(51)Int.Cl. H01L 33/00
H01S 3/18

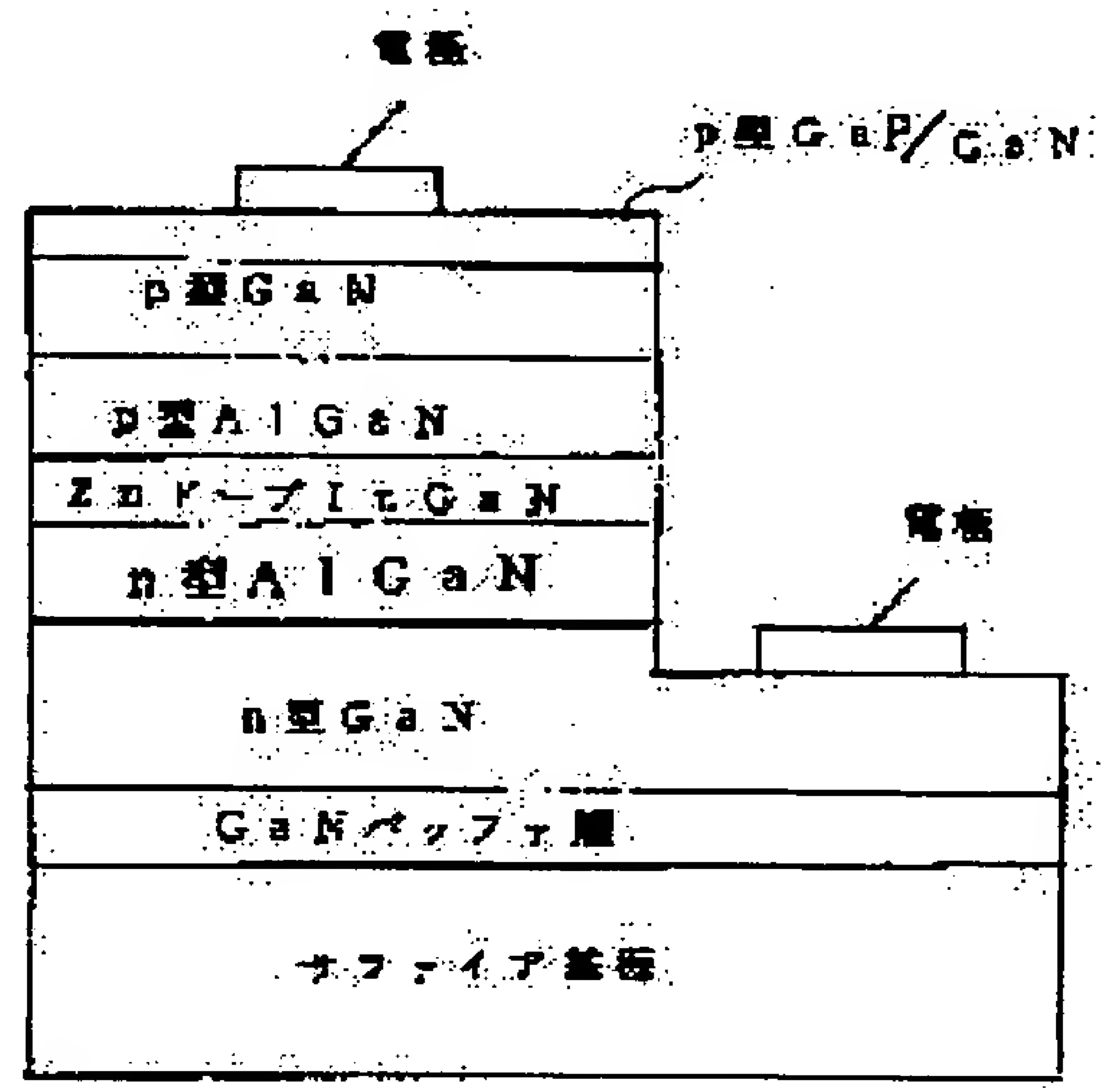
(21)Application number : 07-281959
(22)Date of filing : 30.10.1995

(71)Applicant : MITSUBISHI CHEM CORP
(72)Inventor : SHIMOYAMA KENJI
GOTO HIDEKI

(30)Priority
Priority number : 06265499 Priority date : 28.10.1994 Priority country : JP

(54) SEMICONDUCTOR DEVICE HAVING CONTACT RESISTANCE REDUCING LAYER

(57)Abstract:
PURPOSE: To reduce contact resistance by forming a multilayered film wherein GaPN thin films different in composition are alternately laminated between an AlGeInN based layer and an electrode.
CONSTITUTION: The growth of mixed crystal of GaPN intermediate composition is difficult because of existence miscibility gap. By laminating superlattice composed of Gap rich thin films and GaN rich thin films, band structure equivalent to GaPN bulk can be realized. In order to reduce contact resistance in wide band gap semiconductor, a multilayered film formed by laminating GaP_xN_{1-x} ($x \geq 0.9$) thin films and GaP_yN_{1-y} ($y \leq 0.1$) thin films whose band gaps are small or equal to zero are inserted. Thereby although the carrier concentration can not be made very high, a potential barrier formed between an electrode and a surface layer is remarkably reduced, and ohmic contact is very easily obtained.



LEGAL STATUS

[Date of request for examination]	02.11.2001
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	3605907
[Date of registration]	15.10.2004
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

CLAIMS

[Claim(s)]
[Claim 1] The semiconductor device characterized by having the multilayers which carried out the laminating of 1-GaPxNx (x>=0.9) layer of a thin film, and the GaPyN1-y (y<=0.1) layer of a thin film by turns between the layers and electrodes which consist of an AlGaInN system.
[Claim 2] The semiconductor device according to claim 1 whose thick layer per period of said GaxP1-xN (x>=0.9) layer and a GaPyN1-y (y<=0.1) layer is ten or less molecular layers.
[Claim 3] The semiconductor device according to claim 1 or 2 whose layer which consists of this AlGaInN system is p mold.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] Especially this invention relates to the semiconductor device which reduced especially contact resistance greatly about a semiconductor device about light emitting devices, such as blue which used the gallium nitride system ingredient - green light emitting diode, and blue - green laser diode.
[0002]
[Description of the Prior Art] There is that of a **** better potato in progress of a raise in the brightness of the latest blue and green light emitting diode (LED), and the ZnSSe system and the AlGaInN system are used as an ingredient. When high concentration p mold doping to growth and the GaN system of the quality gallium nitride (GaN) system compound semiconductor film to a substrates top, such as sapphire and SiC, was attained now, the blue light emitting diode of high brightness is realized, and double hetero structure as shown in drawing 2 is used.
[0003]
[Problem(s) to be Solved by the Invention] However, since GaN (Eg=3.39eV) of a wideband gap is used for the surface contact layer, a potential barrier with an electrode tends to become large, and this causes the increment in operating voltage (in the case of drawing 3 and n mold, for Fermi level and EV, the energy of the bottom of a valence band and qphiB are [EC / the energy of the bottom of a conduction band, and EF] a potential barrier). There is the technique of inserting first the layer which carried out the heavy dope directly under an electrode, namely, forming metal-n+-n and the structure metal-p+-p Becoming with such a wideband gap semi-conductor, in order to lower contact resistance (when it is drawing 4 , however n mold). Although hole concentration can dope to the high concentration of 1019 sets in the n mold GaN, on the other hand, it enters only to 1017-set level by the present condition with p mold GaN doping. For this reason, especially the layer that consists of a p mold AlGaInN is difficult for implementation of sufficiently low contact resistance. The increment in this operating voltage leads to generation of heat of a component, and poses a big problem in respect of a life.
[0004]
[Means for Solving the Problem] We hit producing the AlGaInN system LED by MOCVD or the MBE method. The multilayers which carried out the laminating of 1-GaPxNx (x>=0.9) layer of a thin film and the GaPyN1-y (y<=0.1) layer of a thin film for the layer which consists of an InAlGaN system by turns between electrodes are inserted. By inserting said 1-GaPxNx (x>=0.9) layer and 1-GaPxNx (x<=0.1) layer whose thick layer per period is ten or less molecular layers more preferably, it came to solve the above-mentioned technical problem.
[0005] Whether it makes P presentation increase from GaN or makes N presentation increase from GaP, a band gap decreases, and GaPN mixed crystal has the special band structure that a band gap will become zero by middle presentation. However, mixed crystal of a middle presentation is made difficult [growth] for the existence of a MISSHI kinky thread tee gap. Then, the same band structure as GaPN bulk is realizable by carrying out the laminating of the superlattice which consists of GaP Rich's thin film, and GaN Rich's thin film. Then, with a wideband gap semi-conductor, in order to lower contact resistance By inserting the multilayers which carried out the laminating of 1-GaPxNx (x>=0.9) layer of a thin film and the GaPyN1-y (y<=0.1) layer of a thin film which are zero or a band gap is very small by turns Even if it cannot make carrier concentration very high, the potential barrier formed between an electrode and a surface layer is reduced sharply, and it very becomes easy to take ohmic contact (in the case of drawing 5 , however n mold).
[0006] Especially with [the number of the layers of the multilayers in this case] two [more than] (one period), it is not limited, but it is five or more periods preferably. Moreover, what is necessary is just to set it as arbitration in the range which does not produce problems, such as resistance, especially in many parts. In addition, with the layer which consists of an AlGaInN system in this specification, the presentation of aluminum or In shall contain the thing of 0.
[0007] Hereafter, although this invention is explained more to a detail using an example, this invention is not limited to an example, unless the summary is exceeded.
(Example) The configuration of the equipment used for growth of this invention prepares a substrate conveyance room in the center, as shown in drawing 6 , and it has installed one substrate operating room and three reduced pressure MOCVD systems. A deposition chamber 1 is the usual MOCVD system, and is used for growth of an AlGaInN system compound semiconductor. Although a deposition chamber 2 is also the usual MOCVD system, it uses for growth of groups III-V semiconducter other than an AlGaInN system. A deposition chamber 3 can understand a raw material by the radical by microwave excitation, and uses it for the nitriding on the front face of a substrate, and growth of an AlGaInN system compound. A growth procedure is shown for the epitaxial wafer of structure as shown in drawing 1 .
[0008] First, silicon on sapphire is introduced into a deposition chamber 3, and carries out a heating temperature up. In

500-degreeC, radical nitrogen is supplied to a substrate front face by microwave excitation by using nitrogen gas (N2) as a raw material before growth, and the process which makes a surface oxygen (O) atom permute by N atom, i.e., nitriding, is performed. On this front face, 20nm of GaN buffer layers is grown up. Then, a substrate is cooled and a substrate is moved to a deposition chamber 1 through a conveyance room. It heats at the growth temperature C of 1000 degrees, and sequential growth of 4 micrometers of n mold GaN buffer layers, 1 micrometer of n mold aluminum0.2Ga0.8N cladding layers, 0.1 micrometers of Zn dope In0.1Ga0.9N barrier layers, 1 micrometer of p mold aluminum0.2Ga0.8N cladding layers, and the 1 micrometer of the p mold GaN contact layers is carried out on said epitaxial film growth substrate. At this time, hydrogen was used for carrier gas and trimethylgallium (TMG), trimethylaluminum (TMA), and trimethylindium (TMI) were used for III group material gas. Although ammonia (NH3) is generally used for V group raw material, organic metals, such as dimethylhydrazine with the sufficient decomposition effectiveness in low temperature and horse mackerel-ized ethyl, may be used for reduction of growth temperature. Si or germanium was used for n mold dopant, and Mg or Zn was used for p mold dopant. If needed, it continues after growth, and heat-treats in the growth interior of a room, and a carrier is activated. Then, a substrate is cooled and a substrate is moved to a deposition chamber 2 through a conveyance room. A substrate is heated to 700-degreeC and the superlattice which carried out 10 period laminating of GaP of thickness 1 molecular layer and the GaN of thickness 3 molecular layer by turns on said epitaxial film growth substrate is grown up as a contact resistance reduction layer. At this time, hydrogen was used for carrier gas and NH3 and a phosphine (PH3) were used for V group raw material for TMG at III group material gas. Although said GaP0.25N0.75 contact-resistance reduction layer will enlarge the absorption of light which emitted light when it was made not much thick, it is very effective in reduction of contact resistance like the above-mentioned example also at a very thin thin film without the effect of light absorption. Moreover, since this contact resistance reduction layer has very small resistivity, the role which extends a current on a front face is also given sure enough.

[0009] Thus, the electrode was formed in the front-face side and the grown-up epitaxial wafer was processed into the chip. When this chip was assembled as light emitting diode and made to emit light, in 20mA of forward current, the luminescence wavelength of 420nm, and 800 microwatts of radiant power outputs and a very good value were acquired. At this time, operating voltage was 3.4V and operating voltage was 4.0V in the conventional light emitting diode in which the electrode was formed on the p-GaN front face produced for the comparison. Reduction of this operating voltage meant the fall of generation of heat of the component itself, and has improved the life of a component greatly.

[0010] Although the above-mentioned example was about light emitting diode, it cannot be overemphasized as well as there being the same effectiveness also as semiconductor laser that improvement in the same property is obtained also in other semiconductor devices.

[0011]

[Effect of the Invention] When the semiconductor device which reduced resistance between an AlGaInN system semi-conductor layer and an electrode is obtained and this is used as luminescence equipment by this invention, operating voltage can be reduced greatly and the property of the AlGaInN system light emitting device of ultraviolet - red and the life of a component can also be improved sharply.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] Drawing 1 is the explanatory view showing an example of the semiconductor device of this invention.
[Drawing 2] Drawing 2 is the explanatory view showing an example of the conventional semiconductor device.
[Drawing 3] Drawing 3 is the explanatory view of the energy band at the time of installing a direct electrode on the conventional AlGaInN system semi-conductor layer.
[Drawing 4] Drawing 4 is the explanatory view of the energy band at the time of preparing a heavy dope layer on the conventional AlGaInN system semi-conductor layer, and installing an electrode on it.
[Drawing 5] Drawing 5 is the explanatory view of the energy band at the time of inserting the multilayers which carried out the laminating of 1-GaPxNx (x>=0.9) layer of a thin film, and the GaPyN1-y (y<=0.1) layer of a thin film by turns, and installing an electrode on the AlGaInN system semi-conductor layer of this invention.
[Drawing 6] Drawing 6 is the explanatory view of a manufacturing installation used in the example 1.

[Translation done.]

(19)日本国特許庁（ＪＰ）　(12) 公開特許公報(A)　(11)特許出願公開番号

特開平8－213651

(43)公開日　平成８年(1996)８月20日

(51)Int.Cl.[6]	識別記号	庁内整理番号	ＦＩ	技術表示箇所
Ｈ０１Ｌ　33/00	Ａ			
	Ｃ			
Ｈ０１Ｓ　3/18				

審査請求　未請求　請求項の数３　ＯＬ　（全４頁）

(21)出願番号　特願平7－281959

(22)出願日　平成７年(1995)10月30日

(31)優先権主張番号　特願平6－265499

(32)優先日　平６(1994)10月28日

(33)優先権主張国　日本（ＪＰ）

(71)出願人　000005968
三菱化学株式会社
東京都千代田区丸の内二丁目５番２号

(72)発明者　下山　謙司
茨城県牛久市東猫穴町1000番地　三菱化学株式会社筑波事業所内

(72)発明者　後藤　秀樹
茨城県牛久市東猫穴町1000番地　三菱化学株式会社筑波事業所内

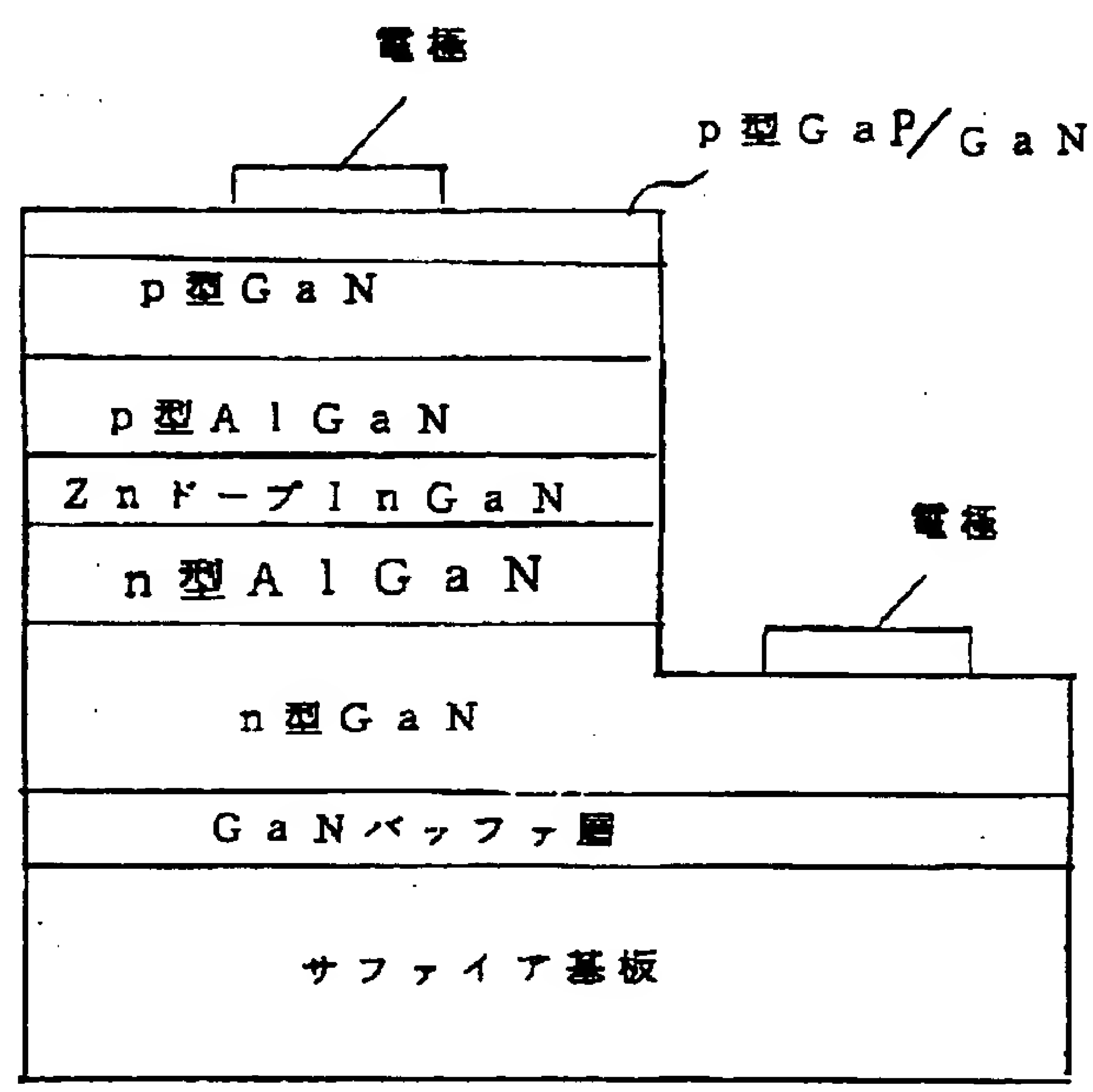
(74)代理人　弁理士　長谷川　曉司

(54)【発明の名称】　コンタクト抵抗低減層を有する半導体装置

(57)【要約】

【課題】　ＡｌＧａＩｎＮ系からなる層と電極との間の抵抗値を低減することにより、特性の向上した半導体装置、特に高輝度の青又は緑色の半導体発光装置を提供する。

【解決手段】　ＡｌＧａＩｎＮ系からなる層と電極との間に薄膜のGaP_xN_{1-x}（$x\geqq0.9$）層と薄膜のGaP_yN_{1-y}（$y\leqq0.1$）層を交互に積層した多層膜を有することを特徴とする半導体装置。



【特許請求の範囲】

【請求項1】AlGaInN系からなる層と電極との間に薄膜のGaP_xN_{1-x}（x≧0.9）層と薄膜のGaP_yN_{1-y}（y≦0.1）層を交互に積層した多層膜を有することを特徴とする半導体装置。

【請求項2】前記$Ga_xP_{1-x}N$（x≧0.9）層及びGaP_yN_{1-y}（y≦0.1）層の1周期当りの厚層が10分子層以下である請求項1記載の半導体装置。

【請求項3】該AlGaInN系からなる層がp型である請求項1又は2記載の半導体装置。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は半導体装置に関し、特に窒化ガリウム系材料を使用した青色～緑色発光ダイオード、青色～緑色レーザーダイオード等の発光素子に関し、特に接触抵抗を大きく低減した半導体装置に関する。

【0002】

【従来の技術】最近の青色及び緑色の発光ダイオード（LED）の高輝度化の進展には目ざましいものがあり、材料として、ZnSSe系やAlGaInN系が用いられている。現在、サファイア、SiCなどの基板上への高品質な窒化ガリウム（GaN）系化合物半導体膜の成長とGaN系への高濃度p型ドーピングが可能となったことにより、高輝度の青色発光ダイオードが実現されており、図2に示すようなダブルヘテロ構造が用いられている。

【0003】

【発明が解決しようとする課題】しかしながら、表面コンタクト層にワイドバンドギャップのGaN（Eg＝3.39eV）を用いているために、電極との電位障壁が大きくなりやすく、このことが動作電圧の増加を招いてしまう（図3、n型の場合、E_cは伝導帯の底のエネルギー、E_Fはフェルミ準位、E_vは価電子帯の底のエネルギー、$q\phi_B$は電位障壁）。このようなワイドバンドギャップ半導体で、接触抵抗を下げるには、まず、ヘビードープした層を電極直下に挿入する、すなわちmetal-n+-n、metal-p+-pなる構造を形成する手法がある（図4、ただし、n型の場合）。n型GaNではホール濃度が10^{19}台という高濃度までドーピングが可能であるが、一方p型GaNドーピングでは、現状では10^{17}台レベルまでしか入らない。このために、特にp型AlGaInNからなる層とは、充分低い接触抵抗の実現は困難である。この動作電圧の増加は、素子の発熱につながり、寿命の点で大きな問題となる。

【0004】

【課題を解決するための手段】我々は、MOCVDやMBE法でAlGaInN系LEDを作製するにあたり、InAlGaN系からなる層を電極との間に薄膜のGaP_xN_{1-x}（x≧0.9）層と薄膜のGaP_yN_{1-y}（y≦0.1）層を交互に積層した多層膜を挿入すること、より好ましくは1周期当りの厚層が10分子層以下である前記GaP_xN_{1-x}（x≧0.9）層及びGaP_xN_{1-x}（x≦0.1）層を挿入することにより、上記の課題を解決するに至った。

【0005】GaPN混晶はGaNからP組成を増加させても、またGaPからN組成を増加させてもバンドギャップが減少し、中間組成でバンドギャップがゼロになってしまうという特殊なバンド構造を有している。しかし、中間組成の混晶は、ミッシビリティギャップの存在のため、成長が困難とされている。そこで、GaPリッチの薄膜とGaNリッチの薄膜からなる超格子を積層することにより、GaPNバルクと同様なバンド構造を実現することができる。そこで、ワイドバンドギャップ半導体で、接触抵抗を下げるために、非常にバンドギャップが小さいもしくはゼロである、薄膜のGaP_xN_{1-x}（x≧0.9）層と薄膜のGaP_yN_{1-y}（y≦0.1）層を交互に積層した多層膜を挿入することにより、キャリア濃度を非常に高くすることができなくても、電極と表面層との間で形成される電位障壁が大幅に低減され、オーミックコンタクトを非常に取り易くなる（図5、ただし、n型の場合）。

【0006】この場合の多層膜の層の数は、2（1周期）以上であれば特に限定されないが、好ましくは5周期以上である。又、多い分には特に抵抗等の問題を生じない範囲で、任意に設定すればよい。尚、本明細書においてAlGaInN系からなる層とは、Al又はInの組成が0のものを含むものとする。

【0007】以下、本発明を実施例を用いてより詳細に説明するが、本発明はその要旨を超えない限り、実施例に限定されるものではない。

（実施例）本発明の成長に使用した装置の構成は図6に示すように中央に基板搬送室を設け、基板交換室1室と減圧MOCVD装置3台を設置してある。成長室1は通常のMOCVD装置であり、AlGaInN系化合物半導体の成長に用いる。成長室2も通常のMOCVD装置であるがAlGaInN系以外のIII－V族化合物半導体の成長に用いる。成長室3は、原料をマイクロ波励起によりラジカル分解することができ、基板表面の窒化及びAlGaInN系化合物の成長に用いる。図1に示すような構造のエピタキシャルウエハを成長手順を示す。

【0008】まずサファイア基板を成長室3に導入し、加熱昇温する。500°Cにおいて、成長前に窒素ガス（N_2）を原料として、マイクロ波励起によりラジカル窒素を基板表面に供給し、表面の酸素（O）原子をN原子と置換させる工程、すなわち窒化を行う。この表面上に、GaNバッファ層20nmを成長させる。この後、基板を冷却し、搬送室を経て成長室1へ基板を移動させる。成長温度1000°Cで加熱し、前記エピタキシャ

ル膜成長基板上に、n型ＧａＮバッファ層４μm、n型$Al_{0.2}Ga_{0.8}N$クラッド層１μm、Ｚｎドープ$In_{0.1}Ga_{0.9}N$活性層０．１μm、p型$Al_{0.2}Ga_{0.8}N$クラッド層１μm、p型ＧａＮコンタクト層１μmを順次成長させる。このとき、キャリアガスに水素を用いて、ＩＩＩ族原料ガスに、トリメチルガリウム（ＴＭＧ）、トリメチルアルミニウム（ＴＭＡ）、トリメチルインジウム（ＴＭＩ）を用いた。Ｖ族原料には、一般的にはアンモニア（NH_3）が用いられるが、成長温度の低減のために、低温での分解効率のよいジメチルヒドラジンやアジ化エチルなどの有機金属を用いてもよい。n型ドーパントには、ＳｉまたはＧｅを、p型ドーパントには、ＭｇまたはＺｎを用いた。必要に応じて、成長後に引き続いて成長室内で熱処理を行い、キャリアを活性化させる。この後、基板を冷却し、搬送室を経て成長室２へ基板を移動させる。基板を７００°Ｃに加熱し、前記エピタキシャル膜成長基板上に厚み１分子層のＧａＰと厚み３分子層のＧａＮを交互に１０周期積層した超格子を接触抵抗低減層として成長させる。このとき、キャリアガスに水素を用いて、ＩＩＩ族原料ガスに、ＴＭＧをＶ族原料には、NH_3及びホスフィン（PH_3）を使用した。前記$GaP_{0.25}N_{0.75}$接触抵抗低減層は、余り厚くすると発光した光の吸収を大きくしてしまうが、上記実施例のように、光吸収の影響のない非常に薄い薄膜でも接触抵抗の低減に、非常に有効である。また、この接触抵抗低減層は、抵抗率が非常に小さいために、表面で電流を広げる役割も果たしてくれる。

【０００９】このようにして成長したエピタキシャルウエハを表面側に電極を形成し、チップに加工した。このチップを発光ダイオードとして組み立てて発光させたところ、順方向電流２０ｍＡにおいて、発光波長４２０ｎｍ、発光出力８００μＷと非常に良好な値が得られた。このとき動作電圧は３．４Ｖであり、比較のために作製したｐ－ＧａＮ表面上に電極を形成した従来の発光ダイオードでは動作電圧が４．０Ｖであった。この動作電圧の低減は、素子自体の発熱の低下を意味し、素子の寿命を大きく改善できた。

【００１０】上記実施例は、発光ダイオードについてであったが、半導体レーザにも同様な効果があることはもちろん、他の半導体装置においても同様の特性の向上が得られることは言うまでもない。

【００１１】

【発明の効果】本発明により、ＡｌＧａＩｎＮ系半導体層と電極の間の抵抗を低減した半導体装置が得られ、これを発光装置として用いた場合には、動作電圧を大きく低減することができ、紫外～赤色のＡｌＧａＩｎＮ系発光素子の特性及び素子の寿命も大幅に改善できる。

【図面の簡単な説明】

【図１】図１は、本発明の半導体装置の一例を示す説明図である。

【図２】図２は従来の半導体装置の一例を示す説明図である。

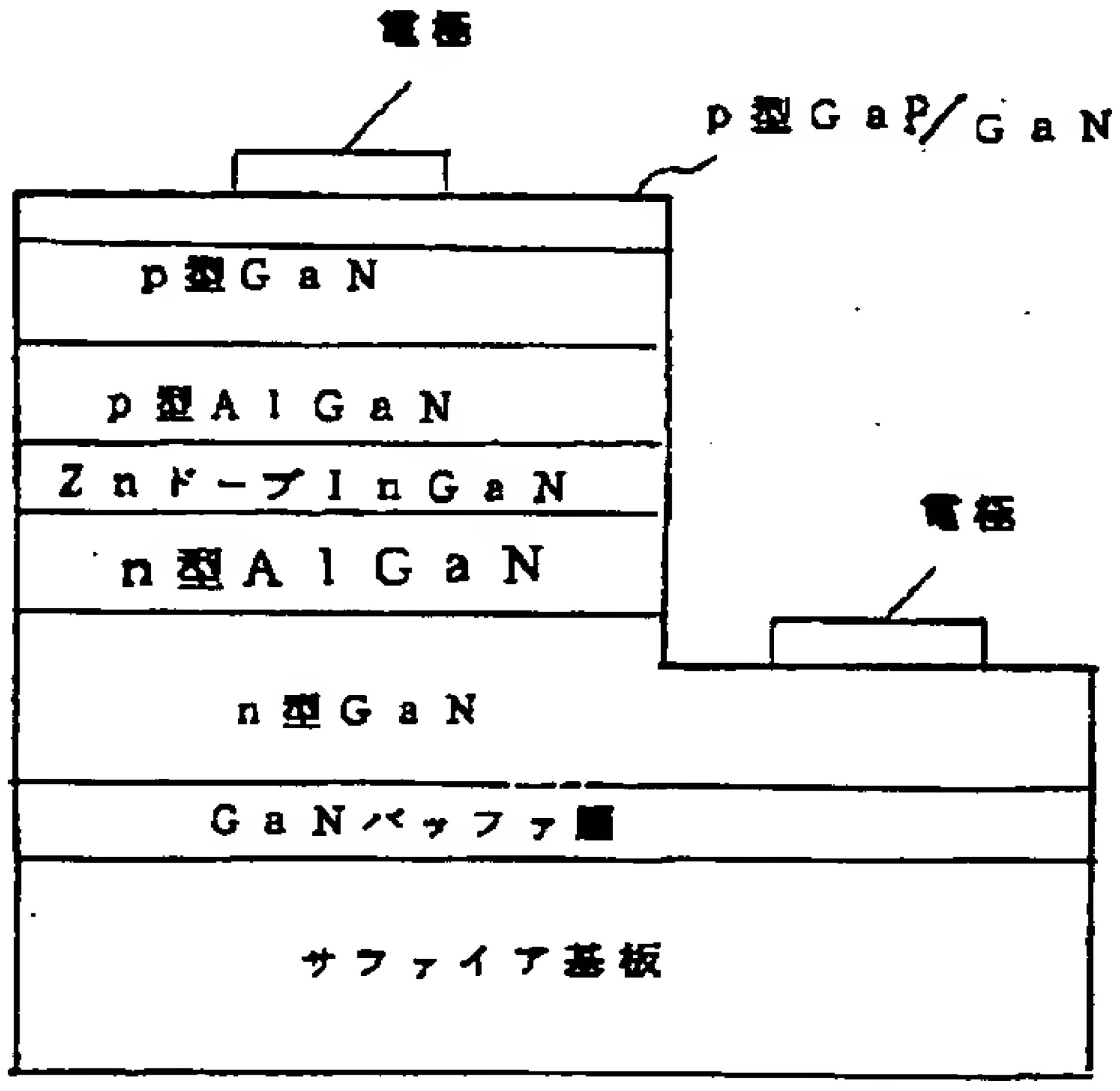
【図３】図３は、従来のＡｌＧａＩｎＮ系半導体層の上に直接電極を設置した場合のエネルギーバンドの説明図である。

【図４】図４は、従来のＡｌＧａＩｎＮ系半導体層の上にヘビードープ層を設けその上に電極を設置した場合のエネルギーバンドの説明図である。

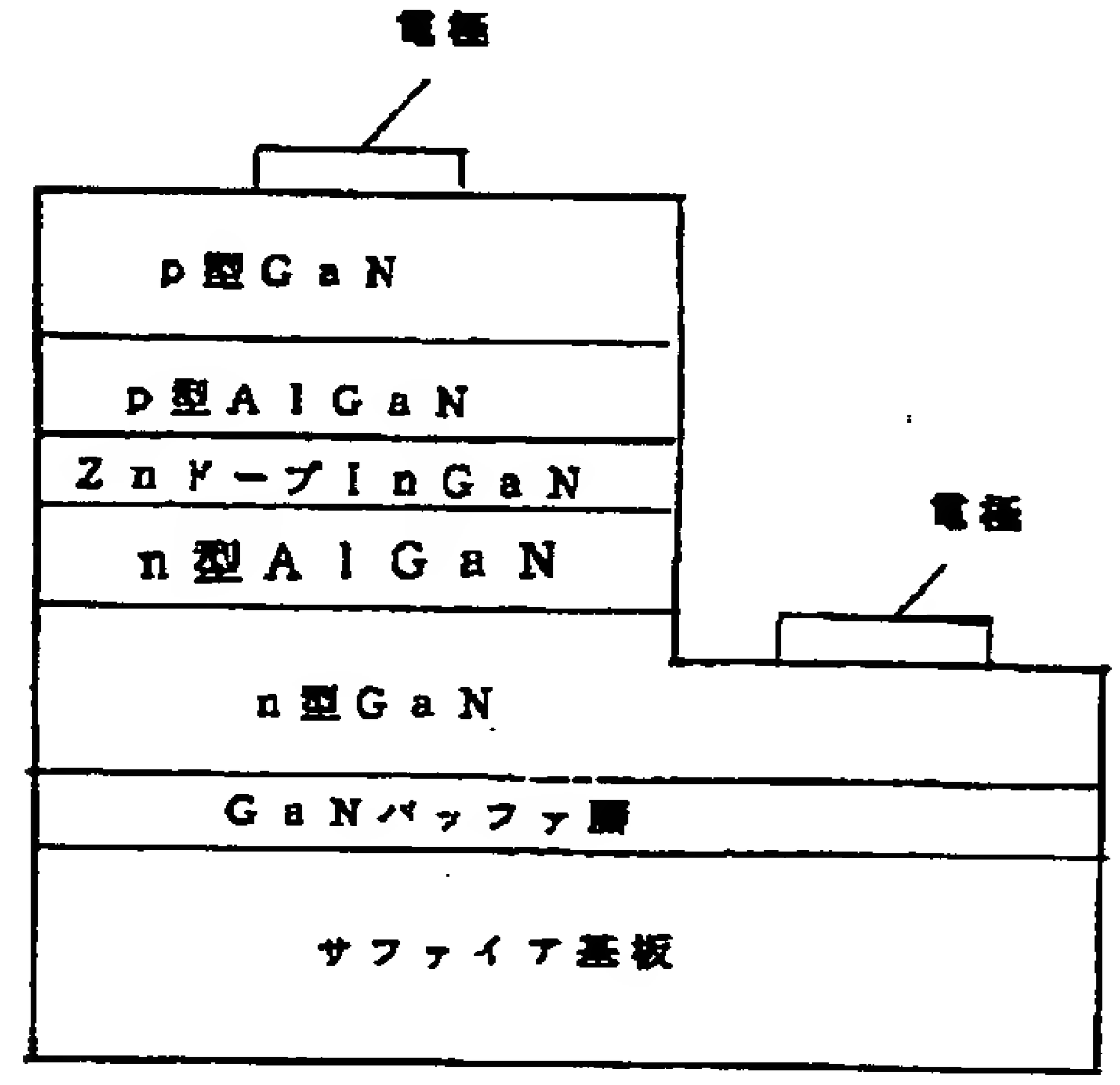
【図５】図５は、本発明のＡｌＧａＩｎＮ系半導体層の上に薄膜のGaP_xN_{1-x}（$x \geqq 0.9$）層と薄膜のGaP_yN_{1-y}（$y \leqq 0.1$）層を交互に積層した多層膜を挿入して電極を設置した場合のエネルギーバンドの説明図である。

【図６】図６は、実施例１で用いた製造装置の説明図である。

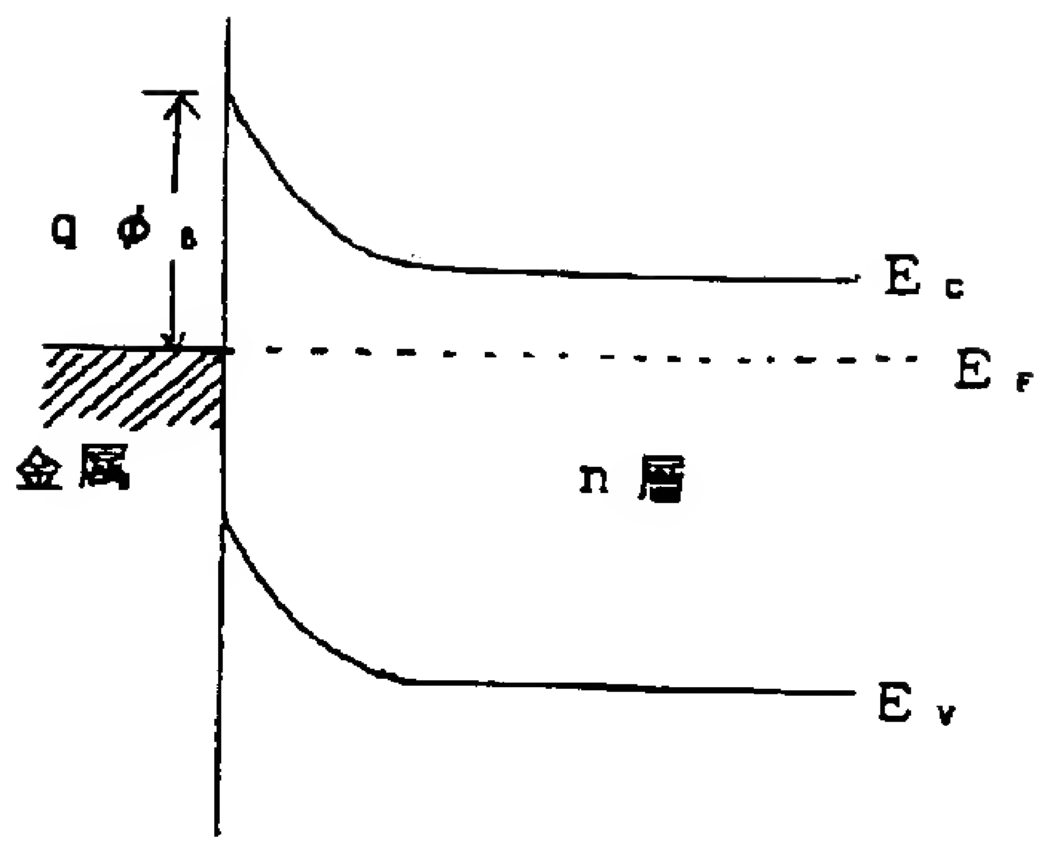
【図１】



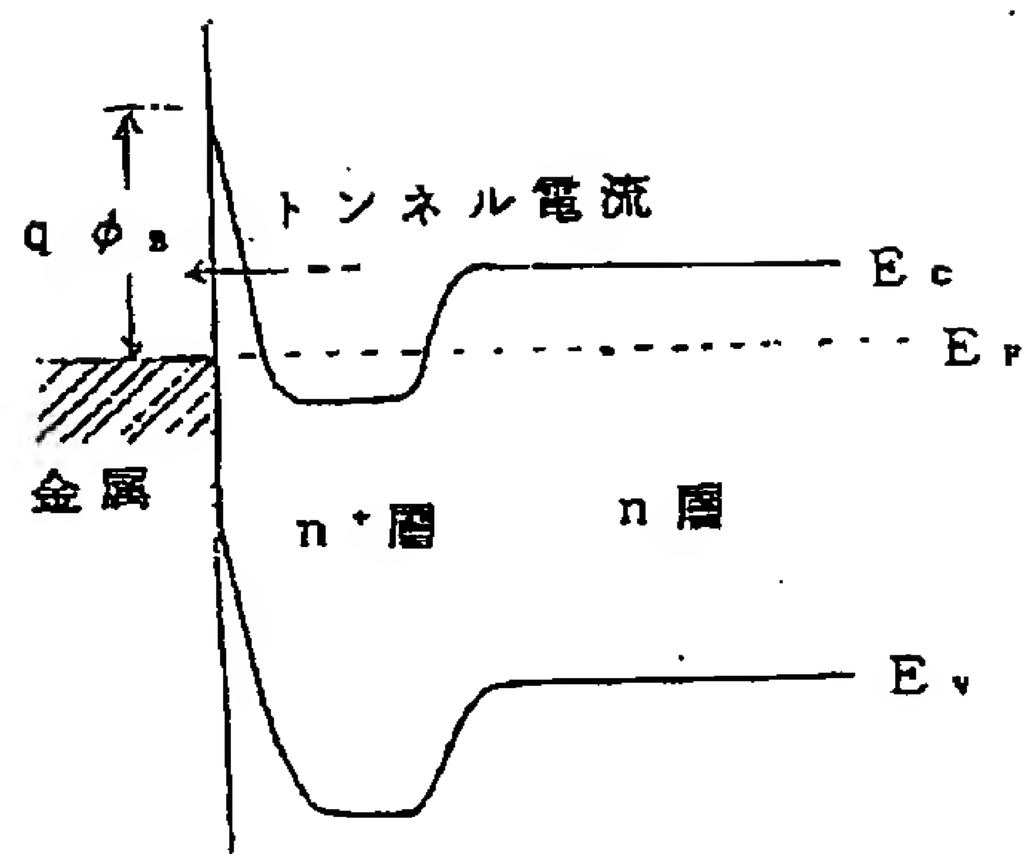
【図２】



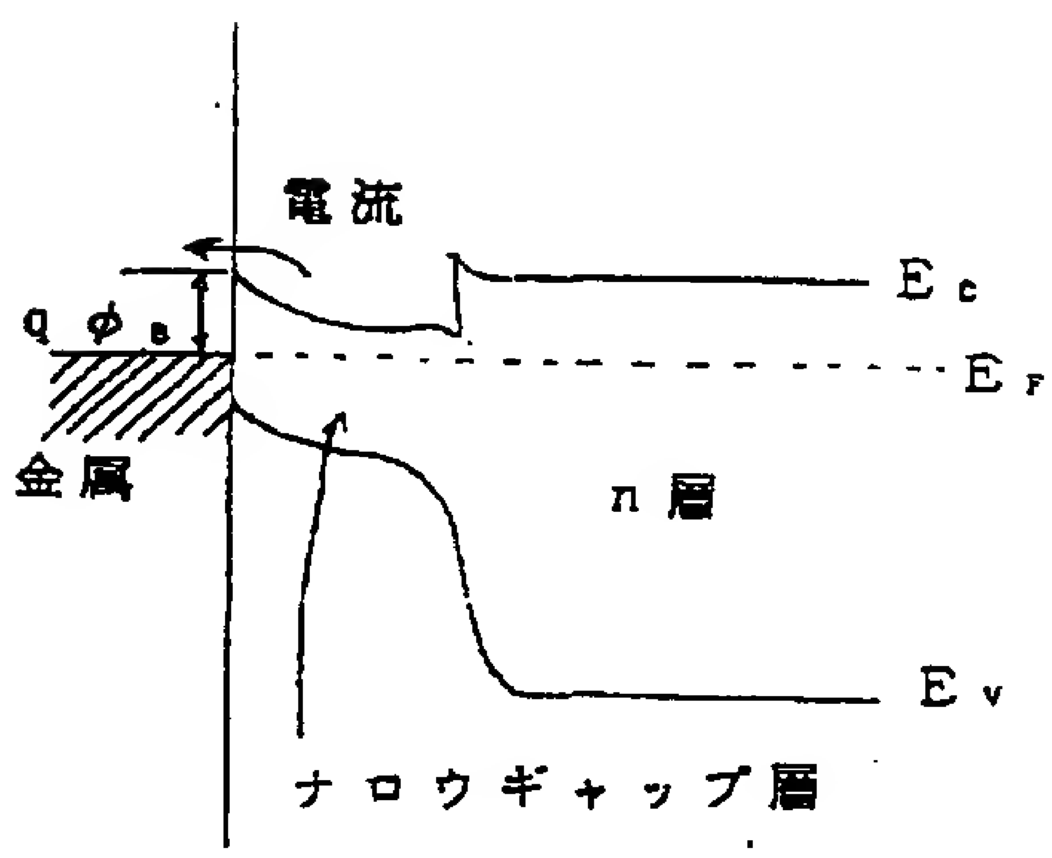
【図3】


qφB
Ec
EF
金属
n層
Ev

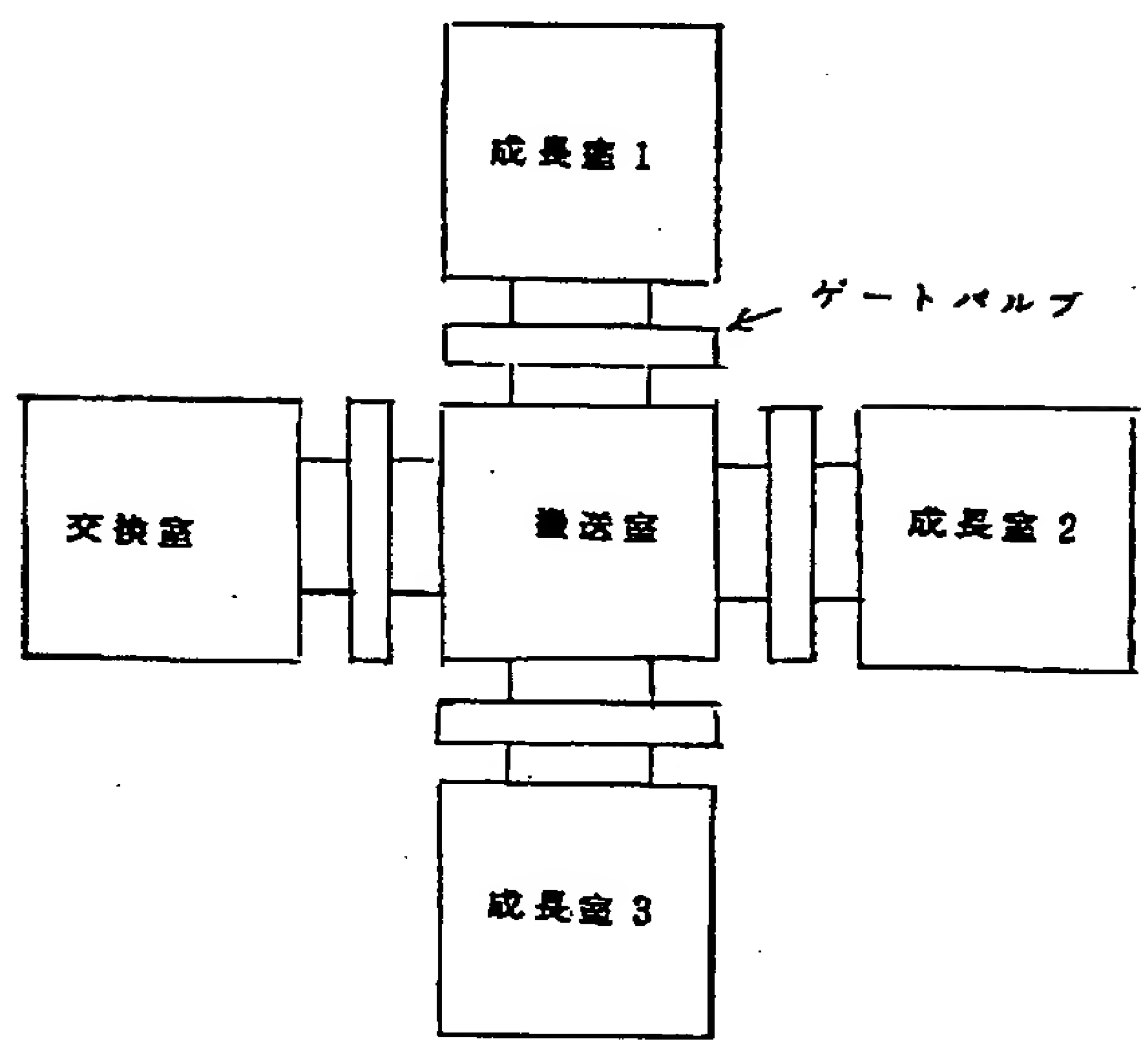
【図4】


qφB
トンネル電流
Ec
EF
金属
n⁺層
n層
Ev

【図5】


電流
qφB
Ec
EF
金属
n層
Ev
ナロウギャップ層

【図6】


成長室1
ゲートバルブ
交換室
搬送室
成長室2
成長室3